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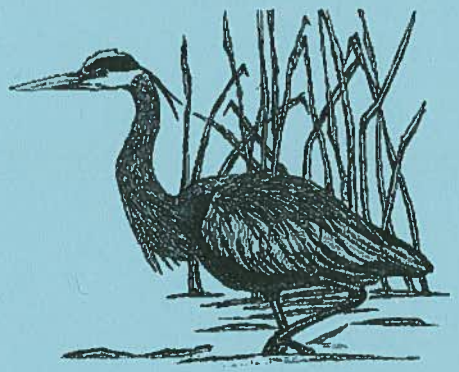
PESTICIDE EVALUATION FOR FLINT HILLS NATIONAL WILDLIFE REFUGE IN KANSAS



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November 2003

PESTICIDE EVALUATION
FOR
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by

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ABSTRACT

Flint Hills National Wildlife Refuge is an overlay on the Corps of Engineers John Redmond Reservoir in east-central Kansas. The Refuge is managed to provide spring and fall habitat and food for migrating shorebirds and waterfowl. Water from the Neosho River, which supplies John Redmond Reservoir, is of fair quality. Contaminants in it are largely from off-site and diverse sources. River water pumped to wetland cells on the north side of the Refuge drain from agricultural areas as well as oil production and storage facilities in the northern portion of the watershed. In addition, several pipelines cross the north side of the Refuge. Thus, contaminants can enter the Refuge through the surface water, and accumulate in sediments and migratory bird foods within the Refuge impoundments. Although, managers of FHNWR suspect agricultural chemicals may be present in the water entering the Refuge, the water has not previously been tested for contaminants. The purpose of this project was to evaluate agriculture and oil-related contaminant inputs to the Refuge and develop a GIS database for management use. This project was conducted over a three year period.

This study's sampling design was not intensive, and therefore is not a conclusive evaluation of contaminant sources and loads into FHNWR. However, the data can be a useful screen for future investigations.

Waterborne concentrations of atrazine, 2,4-D, and alachlor compounds were found in surface waters entering FHNWR in 1997. In 1999, only one site had a detection of any pesticide compound. Low concentrations of aliphatic hydrocarbons and polycyclic aromatic hydrocarbons were infrequently detected in sediments and benthic invertebrates. Only one organochlorine contaminant (dicamba) was detected and that was found in only one sample

A major limitation to this study includes the lack of repeat sampling within a time period. Also, we were unable to precisely time sampling with precipitation events. We most likely did not detect the maximum concentrations that occurred during a sampling period. Therefore, our data probably does not represent the full range or duration of pesticide loadings to FHNWR.

ABBREVIATIONS AND CONVERSION FACTORS

COE = Corps of Engineers
KDHE = Kansas Department of Health and Environment
KDWP = Kansas Department of Wildlife and Parks
FHNWR = Flint Hills National Wildlife Refuge
DOI = Department of the Interior

MSL = mean sea level
ELISA = enzyme-linked immunosorbent assays
GIS = Geographic Information System
BEST = Biomonitoring Environmental Status and Trends
PAHs = Polycyclic Aromatic Hydrocarbons
AHs = Aliphatic Hydrocarbons
OCs = Organochlorines
OPs = Organophosphates
CAHs = chlorophenoxy acid herbicide
AAS = atomic absorption spectrometry

ND = not detected (i.e. Below analytical detection limits)
NA = not analyzed (i.e. No test for this element or compound)

ml = milliliter
g = gram
C = degrees Celsius

PPM = ppm = parts per million = mg/l = µg/g = mg/kg
PPB = ppb = parts per billion = µg/l = ng/g = µg/kg

ACKNOWLEDGMENTS

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INTRODUCTION

Flint Hills National Wildlife Refuge (FHNWR) (Figure 1) is an overlay on the Corps of Engineers John Redmond Reservoir in east-central Kansas. The Refuge is managed to provide spring and fall habitat and food for migrating shorebirds and waterfowl. Water from the Neosho River, which supplies John Redmond Reservoir, is of fair quality (Allen *et al.* 1995). Contaminants in the Neosho River are largely from off-site and diverse sources (Arruda *et al.* 1987, Morrissey and Edds 1994). Water in the impoundments on the north side of the Refuge come from agricultural areas as well as oil production and storage facilities. In addition, several pipelines cross the north side of the Refuge. Thus, contaminants can enter the Refuge through the surface water, and accumulate in sediments and migratory bird foods within the Refuge impoundments. Although, managers of FHNWR suspect agricultural chemicals may be present in the water entering the Refuge, the water has not previously been tested for contaminants. The purpose of this study was to evaluate agriculture and oil-related contaminant inputs to the Refuge and also to develop a GIS database that would enhance future management. GIS databases of FHNWR will be useful in planning future contaminants monitoring and in responding to the needs of the Biomonitoring Environmental Status and Trends (BEST) program.

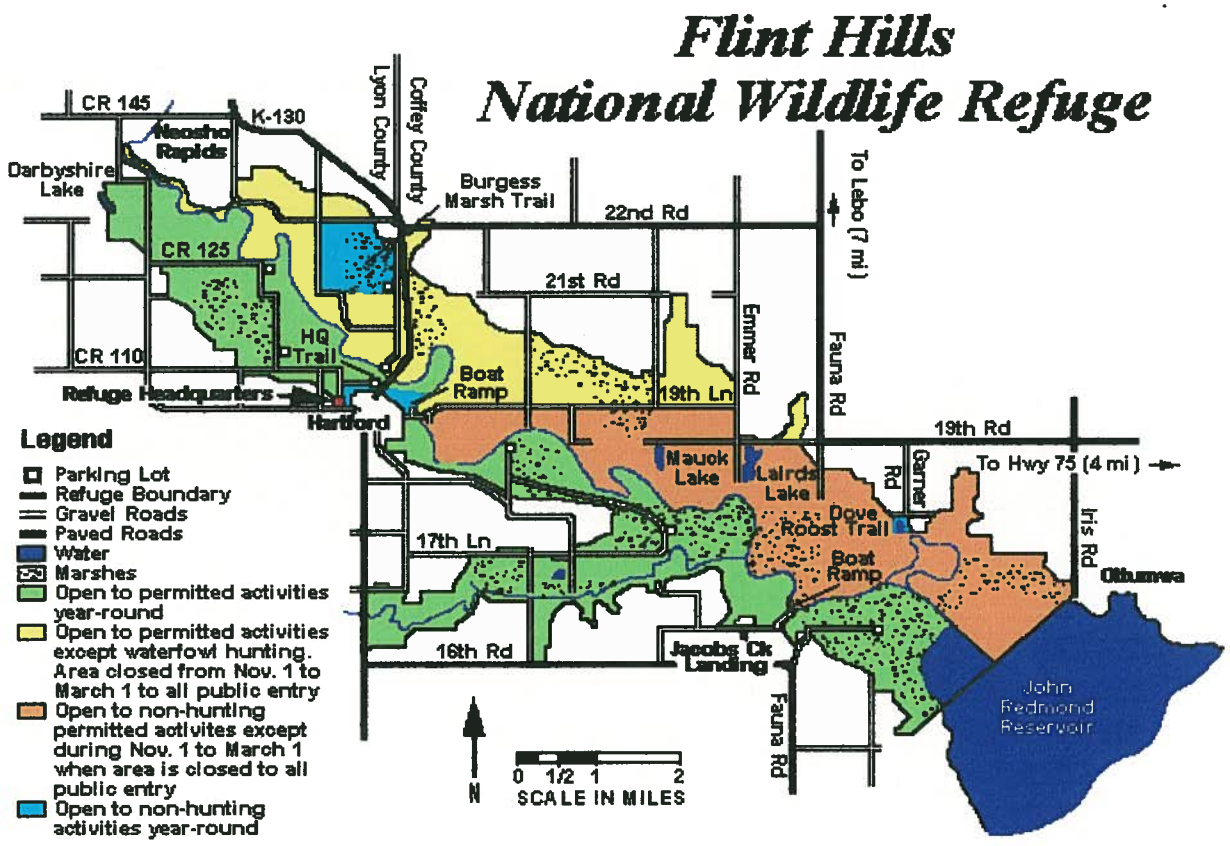

Figure 1. Flint Hills National Wildlife Refuge, Kansas

STUDY AREA

FHNWR is located in the broad, flat Neosho River Valley in Lyon and Coffey counties of east-central Kansas. The Refuge is named for the gently rolling Flint Hills to the west (Research Management Consultants, Inc. 2000).

FHNWR was established in 1966 and consists of 18,463 acres located at the upper end of John Redmond Reservoir, a flood control reservoir, constructed by the Corps of Engineers (COE). The Refuge is operated under a cooperative agreement with the COE and is managed primarily for migrating and wintering waterfowl in the Central Flyway. Feeding and resting areas for migratory birds are provided through moist soil and cropland management programs. Habitats found on the Refuge consist of 4,572 acres of wetlands, 1,400 acres of open water, 599 acres of riparian wetlands along the Neosho River, 3,917 acres of croplands, 3,200 acres of grasslands, 2,400 acres of woodlands, 2,255 acres of brushlands, and 120 acres of administrative and recreational areas.

The Kansas Department of Wildlife and Parks (KDWP) leases 1,472 acres adjacent to FHNWR. This area is known as the Otter Creek Game Management Area and is managed primarily for game species such as bobwhite quail, mourning dove, wild turkey, cottontail rabbit, squirrel, and white-tailed deer.

The Wolf Creek Nuclear Power Plant, located eight miles east of the Refuge, has contracted with the Kansas Water Office for the majority of the storage capacity of John Redmond Reservoir. Water is pumped from John Redmond Reservoir to the 5,500 acre cooling pond at Wolf Creek.

Eight sampling locations were selected based on the high probability for contaminant loading from adjacent and upstream agricultural areas (Figure 2). Exact sampling locations were recorded using geographic positioning technology. Samples were collected four times during the growing season, in May, June, August and September, the most likely time periods for application of agricultural chemicals on crops grown in the area. Descriptions of sampling sites follow:

Site 1 - A man-made canal used to provide water to the Burgess Marsh area, located south of County Road 130.
Site 2 - Adjacent to 22nd Road, near the northern edge of Troublesome Marsh. The marsh is fed by Troublesome Creek which originates off-Refuge.
Site 3 - An unnamed creek which originates off-Refuge and runs through an area adjacent to Bench Marsh. This site was eliminated from the study after the initial 1997 sampling season due to lack of adequate water flow.
Site 4 - On the northern edge of Bench Marsh.
Site 5 - On Lebo Creek which originates off-Refuge and flows into the Boes Marsh.
Site 6 - On the western edge of the Refuge, adjacent to County Road 110 in Maxwell Marsh.
Site 7 - In Eagle Creek, a large tributary of the Neosho River, which flows through several Refuge marshes before reaching the Neosho River.
Site 8 - In Four Mile Creek, a small tributary of Eagle Creek.

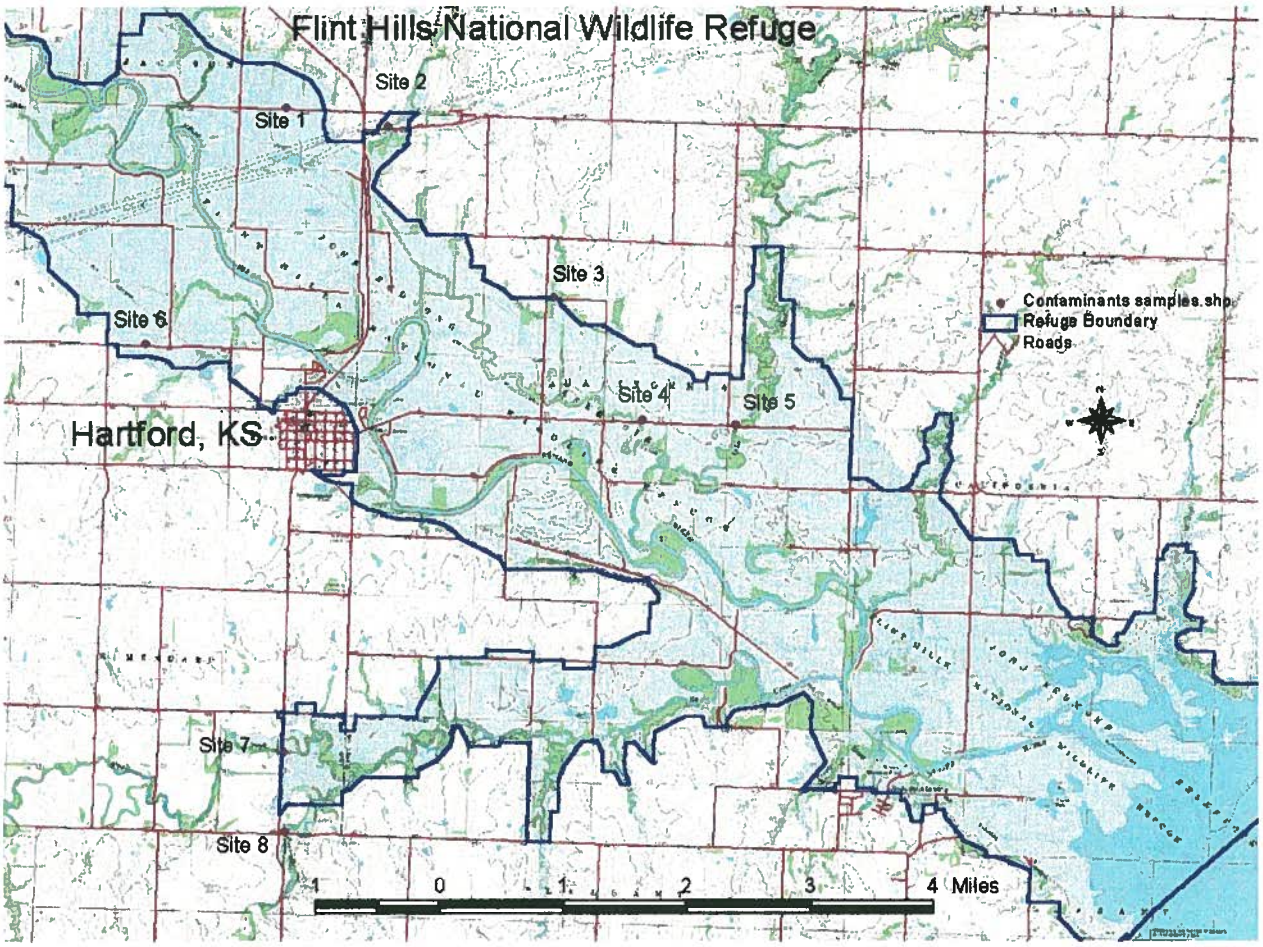

Figure 2. Surface water, sediment, and benthic invertebrate sampling sites at Flint Hills National Wildlife Refuge, Kansas

METHODS

This study was conducted over a three year period from 1997 to 1999. The objective of the first year was to evaluate surface waters at select locations on the Refuge using enzyme-linked immunosorbent assays (ELISA), primarily for agricultural chemicals. ELISA is an inexpensive assay tool, that can be used to screen surface water samples for specific chemical contaminants. The results of the first years efforts allowed investigators to identify contaminant issues and pathways that would be evaluated in more detail during year three of the study. Year two of the study focused on the development of the data layers for the FHNWR geographic information system (GIS). Kansas State University, Manhattan, Kansas was contracted to perform the task of obtaining and developing the data layers for FHNWR.

1997 Sampling Activities

Samples were collected once per month during May, June, August, and September, 1997. A total of 39 samples were collected during this time. Two replicates and two controls were collected for each sampling site and sampling period.

Water samples were collected in 500 ml chemically-clean glass jars with Teflon® lined lids by directly dipping the jar into the water column or by using a Kemmerer horizontal sampler. If the Kemmerer type sampler was used, the first 10-20 ml collected were drained to clear potential contamination of the valve and then transferred into the sample container. The sample jar was filled to the brim, leaving little or no airspace, and analyzed within 24 hours of collection. Equipment was decontaminated after each sample collected, with Alconox® solution and rinsed in deionized water. Decontamination solutions were discarded after use.

ELISA Analysis of Water Samples

Water samples collected in 1997 were analyzed for alachlor, 2,4-D compounds, and atrazine using Ohmicron test kits. This type of testing was used as a screening method to determine if the levels of the compounds present warranted more intensive examination.

The Ohmicron Rapid Assay System applies the principles of ELISA to the determination of the compound. ELISAs are based on the combination of selective antibodies attached to solid support with sensitive enzyme reactions. These features produce an analytical system capable of detecting very low concentrations of chemicals. The immuno-chemical reaction provides high selectivity due to the discriminatory capability of antibodies. The catalytic ability of the enzymes provides highly sensitive detection. The Ohmicron Rapid Assay is based on the use of magnetic particles as the solid support and means of separation. Because the particles are dispersed evenly throughout the reaction mixture, they allow rapid reaction kinetics, provide for precise addition of antibody, and facilitate ease of use.

1999 Sampling Activities

Surface water, sediments, and benthic invertebrates were collected in the third year of the study. We did not find any drainages that were completely unaffected by agricultural chemicals that were suitable for reference sites. Therefore, all the sampling sites used in 1997 were also used in 1999, except Site 3, which ceased flowing in September of 1997.

Water Sampling and Analysis

Surface water was analyzed for organophosphates (OPs), carbamates, chlorophenoxy acid herbicides (CAHs), and trace elements. All samples were analyzed by U.S. Fish and Wildlife Service contract labs. Analytical quality assurance and quality control were managed by Patuxent Analytical Control Facility, Laurel, Maryland.

Each water sample was obtained as previously described for the 1997 screening study. All water samples were collected less than 72 hours after the area had received a one-inch rainfall following an extended dry period.

Three water samples per site were collected in 500 ml amber glass pre-cleaned wide mouthed jars. These water samples were chilled on wet ice and shipped for organic analysis the next day. One water sample per site was collected in a 950 ml HPDE amber container for trace element analysis. Trace element samples were acidified to pH≤2 using a volume of nitric acid adjusted for local buffering capacity.

Water samples collected in the third year of the study were analyzed for OCs, OPs, carbamate pesticides, and CAHs at the Mississippi State Chemical Laboratory (MSCL), Mississippi State University, using the following sample preparation and analysis methods.

Analysis of samples for carbamates was performed on a carbamate analysis system equipped with a WISP model 712 Autosampler. All samples were filtered through 0.45µ nylon filters. Water samples (500 ml) were directly injected into the analytical apparatus. The separation of the analytes occurred at room temperature and the column used was a 3.9 mm X 150 mm Waters nova-par C (4µ). The post-column derivatization was done at 80.0°C. The samples were hydrolyzed with 0.05 m NaOH, then reacted with 0-phthaldialdehyde and 2-mercaptoethenol in 0.05 m sodium borate decahydrate to yield a highly fluorescent isoindole product. The flow from the post-column pumps was 0.5 ml/min. The detector was a Waters 470 scanning fluorescence detector at 339 nm and at 400 nm.

The analysis for OCs, OPs, and CAHs used the following procedures: the sample volume and pH were recorded, 800 ml of the sample were added to a 1000 ml separatory funnel, 100 g of sodium chloride and 50 ml of phosphate buffer were added, then shaken to mix. The pH was adjusted to 8 by adding PRQ 6N KOH or 6N sulfuric acid and shaken for 30 seconds. The sample was allowed to stand one hour at pH 8. The sample container was rinsed with 25 ml CH_2C_{12} and added to the funnel. The remainder of the sample was poured back into the sample container and the graduated cylinder rinsed with 2X25 ml CH_2C_{12}. The sample was shaken and vented for 2 minutes. The CH_2C_{12} was drained through a funnel of CH_2C_{12} and washed with sodium sulfate into a 500 ml french square bottle if there was no emulsion. Otherwise, the lower layer was drained into a centrifuge bottle and centrifuged into separate layers. This was repeated twice. The combined extract contained the organochlorine and nitrogen/phosphorous (N/P) containing pesticides. The pH was adjusted to ≤2 with the addition of PRQ 6N H_2SO_4. The sample was then extracted with 100 ml/ethyl ether by shaking for two minutes. The water was drained from the separatory funnel, passed through the ether layer, and then through the acidified sodium sulfate into a 500 ml french square bottle. This was repeated twice, and then extracted with a final aliquot of 100 ml petroleum ether. The combined extract contained the CAHs.

Trace elements in water samples were analyzed at Research Triangle Institute (RTI), Research Triangle Park, North Carolina. At RTI, ICP measurements were made using a Leeman Labs Plasma Spec I sequential or ES2000 simultaneous spectrometer. For the analytes arsenic and selenium, Graphite Furnace Atomic Absorption (GFAA) measurements were made using a Perkin-Elmer Zeeman 3030 or 4100ZL atomic absorption spectrometer. For the analyte mercury, cold vapor atomic absorption (CVAA) was used with SNC_{14} as the reducing agent. For each analyte, a 50 ml water sample was heated in a capped 120 ml Teflon vessel in the presence of 5 ml of Baker Instra-Analyzed nitric acid for fifteen minutes at 300 watts in a CEM microwave oven. The sample was then diluted to 50 ml with laboratory pure water and analyzed.

The analytical methodology for organochlorine pesticides, N/P pesticides, trace elements, aliphatic and polycyclic aromatic hydrocarbons in surface water reported concentrations for the analytes listed in Table 1.

Sediment Sampling and Analysis

Two sediment samples per site were collected in pre-cleaned 250 ml clear glass jars. Composite samples were taken with a stainless steel spoon or ponar dredge. The samples were mixed thoroughly in a stainless steel bucket or pan and then transferred to the sample jars. Jars were filled approximately three-fourths full to allow for expansion during freezing. Samples were placed on ice in the field and stored at -20°C upon return to the field office until shipment to contract labs. All sampling devices were decontaminated after each site.

A total of sixteen composite sediment samples were collected. The samples were divided between the two contract labs for analysis. Eight of the samples were analyzed for OCs, PAHs, and aliphatic hydrocarbons (AHs) at MSCL. The other eight composite sediment samples were analyzed at Geochemical & Environmental Research Group (GERG), Texas A&M for trace elements.

MSCL used the following sample preparation and analysis methods for OPs, PAHs, and AHs. A 20 g subsample was extracted using acetone followed by petroleum ether, with a one hour soak in each solvent and intermittent shaking. A final acetone/petroleum ether extraction was performed and the extracts combined, centrifuged, and transferred to a separatory funnel containing sufficient water to facilitate partitioning of residues into the petroleum ether portion. The petroleum ether was washed twice with water and concentrated using a Kuderna-Danish evaporator to an appropriate volume. An aliquot of the concentrated extract for pesticide determination was transferred to a 1.6 g Florisil mini-column topped with 1.6 g sodium sulfate. Residues were eluted from the column in two elution fractions. Fraction 1 consisted of 12 ml hexane followed by 12 ml of 1% methanol in hexane and Fraction II consisted of an additional 24 ml of 1% methanol in hexane. Quantification of residues in the two Florisil fractions and three Silicic acid fractions was by packed or megabore column, using electron capture gas chromatography. A second aliquot of the concentrated extract for hydrocarbon determination was transferred to a 20 g 1% deactivated silica gel column topped with 5 g neutral alumina. AH and PAH residues were fractionated by eluting aliphatics from the column with 100 ml 40% methylene chloride/60% petroleum ether, followed by 50 ml methylene chloride (combined eluates, Fraction II). If needed, Fraction I, containing aliphatics, was subjected to additional cleanup by concentration and transferred to a deactivated (2% water) Florisil column. Aliphatic residues were eluted from the Florisil column using 200 ml of 6% diethyl ether/94% petroleum ether. The eluate was concentrated to an appropriate volume for quantification by capillary column, flame ionization gas chromatography. The silica gel Fraction II, containing aromatic hydrocarbons, was concentrated, reconstituted in methylene chloride, and subjected to gel permeation chromatographic (GPC) cleanup prior to quantification by capillary, flame ionization gas chromatography and fluorescence HPLC.

The analytical methodology for OCs, AHs and PAHs in sediment reported concentrations for the analytes listed in Table 1.

GERG used the following sample preparation and analysis methods. Sediments were digested with aqua regia in glass beakers on a hotplate and diluted to volume with distilled water. The

trace elements in the digestate were determined by three techniques, depending upon concentration and element. Mercury was determined by cold vapor atomic absorption spectrometry (AAS), in which Sn_2^+ is used to reduce HgO. Arsenic, selenium, cadmium, and lead were determined by graphite furnace AAS, in which electrical heating was used to produce an atomic cloud. The remaining elements, and cadmium or lead when in high concentrations, were determined by atomic emission using an argon plasma.

Invertebrate Sampling and Analysis

Samples of composite benthic invertebrates were analyzed for PAHs at the MSCL. Trace elements in benthic invertebrates were analyzed at GERG. Two composite benthic invertebrate samples of 5 to 50 g were collected per site, by hand, net, ponar dredge, multi-sampler plates, or a combination of the above. Species composition in the samples consisted of crayfish, predaceous diving beetles, and other aquatic invertebrates, with the majority of the sample being glass shrimp. The samples were transferred to pre-cleaned glass jars, chilled on ice in the field, and frozen at -20°C upon return to the field office until shipment to contract lab..

A total of sixteen composite invertebrate samples were collected. The samples were divided between the two contract labs for analysis. Eight of the samples were analyzed for PAHs at MSCL. The other eight composite invertebrates samples were analyzed at GERG for trace elements.

For polyaromatic hydrocarbon (PAH) analyses in benthic invertebrates, a sample of appropriate size was digested in 6N aqueous potassium hydroxide for 24 hours at 35°C. The digestate was cooled thoroughly in an ice bath and carefully neutralized with glacial acetic acid. The neutralized reaction mixture was then extracted three times with methylene chloride. The combined extracts were concentrated to near dryness and reconstituted in petroleum ether for transfer to a 20 g 1% deactivated silica gel column, and topped with 5 g neutral alumina. PAH residues were separated by eluting aliphatics from the column with 100 ml petroleum ether (Fraction I) followed by elution of aromatics using 100 ml 40% methylene chloride/60% petroleum ether and then 50 ml methylene chloride (combined eluates, Fraction II). If needed, Fraction I containing aliphatics was subjected to additional cleanup by concentration and transfer to a deactivated (2% water) Florisil column. Aliphatic residues were eluted from the Florisil column using 200 ml 6% diethyl ether/94% petroleum ether. The eluate was concentrated to an appropriate volume for quantification by capillary column, flame ionization gas chromatography. The silica gel Fraction II containing AHs was concentrated, reconstituted in methylene chloride, and subjected to gel permeation chromatography (GPC) cleanup prior to quantification by capillary, flame ionization gas chromatography and fluorescence HPLC.

For trace element analysis in composite benthic invertebrates, tissues were digested in heavy-walled, screw-cap Teflon Bombs with concentrated high purity nitric acid. Bombs were heated in a 129°C oven for 2-8 hours and opened three times to release CO_2 build-up. This procedure resulted in a total digestion for all trace elements. Most metals in the digestate were determined by graphite furnace AAS, in which electrical heating is used to produce an atomic cloud. Some elements were typically in high enough concentrations (i.e. zinc) to be determined by flame AAS. Mercury was determined by cold vapor atomic absorption spectrometry (AAS), in which SN_2^+ is used to reduce HgO.

The analytical methodology for PAHs and trace elements in benthic invertebrates reported concentrations for the analytes listed in Table 1.

RESULTS AND DISCUSSION

Herbicides in Surface Water

Atrazine

Ten of 31 total samples (32%) analyzed in 1997 contained herbicide concentrations above the high quantification range for Atrazine (> 4 µg/l) (Table 2). All ten of these samples were collected in May and June. In May, four of eight samples (50%) had concentrations greater than the high quantification range and in June, six of eight samples (75%) exceeded the high quantification range. Sites 6 and 7 in May, and Site 5 in June had concentrations above the detection range of the test kit. Samples collected in September had the lowest average concentration of all collection periods. The highest concentration detected was 18.7 µg/l found at Site 6 during May. Of the 31 samples collected, 13 (42%) had concentrations greater than 1 µg/l, with all but one being collected during May and June.

Atrazine, a triazine compound, is the most frequently detected pesticide in Kansas surface water (Carney *et al.* 1991). Atrazine is the second most used herbicide, measured in pounds of active ingredient in the United States, with 76-85 million pounds applied each year (EPA 2001). Concentrations between 1 µg/l and 5 µg/l may adversely affect phytoplankton growth and succession, which in turn can adversely affect higher levels of the food chain (Eisler 1989a). Aquatic fauna are indirectly impacted through the reduction of the food supply of herbivores and loss of macrophyte habitat (Eisler 1989a). Atrazine is persistent in surface water and in ground water in high-use areas, and is found in air and rainfall samples far from its use sites (EPA 2001).

2,4-D

The lowest 2,4-D concentration detected was 0.13 µg/l at Site 2 during May. The highest concentration of 2,4-D was found at Site 6 during May (2.38 µg/l). Site 6 had the highest concentrations for May, August, and September. Despite this, none of the 27 samples analyzed had amounts greater than the high quantification range for the compound of concern (100µl)(Table 3).

Although information on sublethal effects of low concentrations of 2,4-D is limited, research has indicated that concentrations >10 µg/l inhibits photosynthesis in sago pondweed by 50% in laboratory experiments (Fleming *et al.* 1995).

Alachlor

One of the 31 samples (3%) analyzed contained alachlor concentrations greater than the concentration of concern (5 µg/l)(Table 4). Site 1 had the highest concentration of any sample (5.05 µg/l) which was higher than the detection range of the test kit and was interpolated by the photometer computer.

Alachlor is water soluble and can readily move to groundwater, especially in sandy soils. In vegetation it is absorbed primarily by germinating shoots and it is readily translocated throughout the plant. Higher concentrations appear in the vegetative parts than in the reproductive parts of the plant. Alachlor is rapidly metabolized to water-soluble products in plants.

Conclusion

Analysis of surface water conducted during 1997 with ELISA field tests kits found agricultural chemicals such as atrazine, 2,4-D, and alachlor were entering the Refuge via the surface water. These chemicals were commonly found in Lebo Creek, Troublesome Creek, Four Mile Creek, Eagle Creek, unnamed creeks, and drainage canals that supply Refuge wetlands. Atrazine was the most frequently detected compound. The compounds were primarily found during the spring and early summer.

Pesticide concentrations and loads in surface waters vary greatly depending on time of use, rainfall timing, intensity, and amounts (Richards and Baker 1993). Peak herbicide concentrations in rivers of the Midwest can occur over days to weeks and may not be detected by a single monthly sample (Larson *et al.* 1997). Due to our sampling frequency and inability to precisely time sampling with precipitation events, we most likely did not detect the maximum concentrations that occurred. Our data also do not represent the full range or duration of these pesticide concentrations.

We did not record consistent detections (>50% each sampling period) for the cholinesterase-inhibiting compounds in 1997, therefore, we did not collect avian samples for residue or brain cholinesterase levels in 1999, as was originally proposed.

Trace Elements in Sediments, Benthic Invertebrates, and Surface Water

Analytical results for trace elements from samples collected in 1999 are shown in Table 5 (sediment), Table 6 (benthic invertebrates), and Table 7 (surface water).

Arsenic

The arsenic concentrations in the 1999 sediment samples were comparable to values found in other studies (Table 8). Compared to sediment concentrations from the North Central United States (Table 8), the concentrations appear elevated. However, when compared to Western United States DOI study areas (Table 8), the arsenic concentrations in the sediments are within the normal range. Background arsenic concentrations in freshwater aquatic biota normally are less than 1 µg/g wet weight (ww) (Eisler 1988a). All of the invertebrate samples in this study, had concentrations less than 1 µg/g ww (Table 6). Arsenic was detected in 42% of the surface water samples, however, the concentrations were low and not at levels considered harmful.

Limited information is available on the biological need for arsenic or on how it affects animal life. Low levels may actually improve health and growth in animals, and inorganic arsenic can protect against the harmful effects of inorganic selenium (Eisler 1988a).

Mercury

Mercury was not found in any of our sediment or surface water samples. It was however, found in 63% of the benthic invertebrate samples. The highest concentration (0.459 µg/l) was found at Site 5 (Table 6).

Mercury is an extremely toxic nonessential metal. It is known to exhibit teratogenic, mutagenic, and a carcinogenic effects. Man-made reservoirs also have led to increased mercury levels in fish because mercury is released from flooded soils to the water (Eisler 1987a). In 1980, the U.S.

Environmental Protection Agency's proposed mercury criteria for freshwater aquatic life protection was 0.00057 µg/l (24-hour average), not to exceed 0.0017 µg/l at any time. This standard seemed to afford a high degree of protection to freshwater biota, as judged by survival, bioconcentration, and biomagnification (Eisler 1987a). The invertebrate samples indicate that some bioaccumulation of mercury may have occurred at the sampling locations.

Selenium

Selenium was not detected in surface water or sediment samples. However, it was detected in benthic invertebrates at all sites in our study (Table 6). Site 4 at FHNWR had the highest concentration of selenium in invertebrates (2710 µg/kg). Background selenium concentrations in aquatic invertebrates ranges from 400 to 4,500 µg/kg, and is typically ≤2,000 µg/kg (U.S. Department of the Interior 1998).

Selenium (Se) is an essential trace element for terrestrial and freshwater organisms, but the range between when Se is essential and when it becomes toxic is very narrow. Migratory waterfowl were adversely affected while nesting at selenium-contaminated irrigation drain water ponds in California and consuming food chain organisms that contained between 12,000 and 280,000 µg/kg of Se (Eisler 1985). Many species of fish and wildlife require high-protein diets for optimal reproduction, and the invertebrate component of the diet is often the principal source of protein. Consequently, selenium-induced alterations of invertebrate density or community structure could have indirect ecological impacts on fish and wildlife populations (U.S. Department of the Interior 1998).

Lead

Detectable concentrations of lead in surface water were found in only one sample (Table 7). Benthic invertebrates analyzed had lead concentrations ranging from 0.753 to 2.53 µg/g dry weight (dw)(Table 6). Sediment samples in this study ranged from 15.4 to 2,408 µg/g dw. Studies suggest that 0.1 to 10 µg/g dw represents toxic levels for several species. Sediment lead concentrations at all eight sites were elevated compared to North-Central United States sediments (Table 8). When compared with Western United States DOI study area (Table 8), site 4 sediment concentration is greatly elevated. Allen (1991) reported elevated lead concentrations in sediments at FHNWR.

The toxicity of lead varies widely among species and the toxicity is affected by many factors including life stage, water quality, and the presence of other elements (Sorenson 1991). Lead is biologically nonessential and has long been recognized as a cumulative poison. The chemistry of lead in aquatic systems is complex and its availability to aquatic organisms varies (Eisler 1988b). Lead concentrations are highest near mining, smelting, and refining sites; lead storage battery recycling plants; areas of high vehicular traffic; urban and industrialized areas; sewage and spoil disposal areas; dredging sites; and areas of heavy hunting pressure (Eisler 1988b). Sediments constitute the largest global reservoir of lead. The most likely sources of lead on the Refuge are lead shot and lead fishing weights. Areas with heavy hunting and fishing use either in the past or present may have elevated lead levels. Future studies may want to focus on residual lead shot in these areas.

Other Trace Elements

Molybdenum was not detected in any sediment or benthic invertebrate samples (Tables 5 and 6). Site 1 had a molybdenum concentration of 0.0045 mg/l in surface water which is below the 10 µg/l recommended safe level for drinking water (Eisler 1989b). Cadmium concentrations in surface water were not detected.

Sediment concentrations of aluminum, iron, and magnesium were not elevated compared to a previous study of FHNWR (Allen 1991). Boron, chromium, copper, nickel, strontium, vanadium and zinc concentrations in sediment samples were low compared to those found in sediments in western United States DOI Drainwater study areas (Table 8). Beryllium, cadmium, and manganese concentrations in sediments from this study were comparable to those found in other studies in the U.S. (Table 8). Barium concentrations in sediment were slightly elevated when compared to DOI Drainwater study areas.

Sediment Sample Composition

Non-polar organic contaminants such as PAHs are adsorbed more strongly to finer grain particles and are therefore less available to biota (Colombo *et al.* 1989). Their availability to biota is also inversely related to total organic carbon concentrations of the soil (Neff 1984). The majority of sediment samples from FHNWR were generally classified as a silty clay loam, with a low organic carbon content (Table 9). These characteristics indicate that the sediments in areas sampled are likely to carry limited quantities of adsorbed organic contaminants, however any organic contaminants present may be readily available.

Aliphatic Hydrocarbons in Sediment

Analysis of the sediment samples showed no n-C14 through n-C16, n-C18, n-C19, n-C32, or n-C34 in many of the samples. The AH, n–tetradecane n-C14, was found in only one sample. In general, low concentrations of aliphatic hydrocarbons were infrequently detected in sediments. Concentrations of AHs in sediment samples are shown in Table 10. Indices used to discern the source of AHs in sediment samples are shown in Table 11.

AHs occur naturally in plants and algae and are found in oil and gas deposits. On release into the environment, the composition and potential toxicity of petroleum mixtures change rapidly and continuously as individual compounds are volatilized, solubilized, dispersed, and degraded at differing rates by physical, chemical, and biological processes. The rates of these weathering processes vary depending on temperature, currents, wind, concentrations of suspended and dissolved components of the receiving water, and biological activity. The timing of petroleum releases relative to the distribution and life cycles of organisms determines the potential exposure and correspondingly, the biological effects of exposure. Ecosystems also vary in their susceptibility to oil (U.S. Geological Survey 2003). Both biogenic (plant derived) and petrogenic (petroleum derived) can be found in the environment. Distinguishing between them is important in the interpretation of hydrocarbon residues in sediments and biota. The sources of petrogenic aromatic and AHs in aquatic systems are generally considered to be from combustion of fossil fuels, antifouling agents such as creosote, and spills or discharges (Connell and Miller 1984, Winger *et al.* 1990 and the citations therein).

Several indices have been found useful to discern the sources of AHs (Colombo *et al.* 1989). The presence of phytane and a series of odd and even number carbon aliphatics is indicative of petrogenic hydrocarbons. The presence of pristane and phytane with relatively low values of C17/Pristane (C17/Pri) and C18/Phytane (C18/Phy) (<3) indicate at least partial petrogenic contamination (Keizer *et al.* 1978). Low C17/Pri and C18/Phy ratios indicate the presence of degraded oil (Colombo *et al.* 1989). Phytane concentrations are usually less than 0.001 µg/l in un-oiled matrices. Concentrations of pristane and phytane (Pri/Phy) are nearly equal in petroleum contaminated samples (Gearing *et al.* 1976). The C16 ratio, which is the sum of all the n-alkanes/nC16, is usually high (i.e. 50) for biogenic materials compared to relatively low values (i.e.15) in oily samples (Colombo *et al.* 1979). Petrogenic compounds have approximately a one to one ratio (1:1) of total odd-carbon alkanes and even carbon alkanes (odd/even) (Tran *et al.* 1997). The carbon preference index (CPI) is calculated by the formula 2(C27+C29)/(C26+2C28+C30). A CPI value of less than 3 indicates contamination by petrogenic sources (Farrington and Tripp 1977).

While the results of the indices (Table 11) do not conclusively identify the predominant source of the hydrocarbons in most of the sediment samples, some conclusions can still be made. The AHs in the sediment sample from Site 4 were inconclusive between biogenic and petrogenic origin. Samples from Sites 1, 7 and 8 met the criteria of two or more of the indices, indicating biogenic origin. While Sites 2, 5 and 6 met the criteria for petrogenic origin in two or more of the indices used.

Polycyclic Aromatic Hydrocarbons in Sediment and Benthic Invertebrates

Only seven aromatic hydrocarbons were detected in sediments (Table 12) and two were detected in benthic invertebrates (Table 13). Of these, all were detected in fewer than 30% of the samples. Only naphthalene was detected in all sediment samples. Sediment samples from Site 6 showed detections of the PAHs benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(e)pyrene, phenanthrene, naphthalene, and perylene. PAHs detected in benthic invertebrates were naphthalene and perylene.

PAHs are a large and diverse group of fused ring aromatic hydrocarbons that are derived from endogenous and anthropogenic sources (Niimi and Palazzo 1986). These environmental contaminants are thought to originate from the incomplete combustion of organic matter. PAHs are problematic due to their propensity to initiate carcinogenic and/or mutagenic effects in terrestrial as well as aquatic biota. Fish, commonly used to monitor numerous contaminants, rapidly biotransform PAHs through activation of a mixed function oxidase enzyme system. This severely limits the correlation of PAH concentrations in fish tissues with exposure concentrations (Buhler and Williams 1989). Generally, PAHs are associated with chronic impacts rather than acute. These impacts are often the result of exposure to low levels of complex mixtures of PAHs rather than exposure to just one compound (Irwin *et al.* 1998).

PAHs in sediments may be assimilated by plants, where they can accumulate and may translocate to the stem, shoots, and leaves. Metabolic degradation of PAHs by soil and sediment microbes can transform PAHs into more hazardous chemicals (Irwin *et al.* 1998). PAHs find their way into aquatic environments through deposition and from PAH contaminated runoff (Neff 1985). Once in the water column PAHs become incorporated into bottom sediments, concentrate in aquatic

biota, or experience chemical oxidation and biodegradation (Eisler 1987b). Local sources of PAHs in FHNWR's environment include prairies fires, vehicle traffic, and spills from oil pipelines.

Organochlorines in Surface Water

Site 6, Maxwell Marsh, was the only site with an organochlorine detected in a surface water sample. Dicamba, the broad-spectrum chlorobenzoic acid herbicide used in large quantities for general weed control on grain crops, pastures, and non-crop areas, was detected at 0.000830 mg/l. A concentration of 1.0 $\mu g/l^{-1}$ is of concern for aquatic life in freshwater (Canadian Environmental Quality Guidelines 2002).

GIS Database

The proposal for this study called for the creation of a GIS database. This database was to be used to determine if there was a possible spatial correlation to the distribution of elevated levels of pesticides on FHNWR and then ascertain if any specific locations could be the likely source of the pesticides. The third use of the GIS database was to determine those areas in which land use management could reduce pesticide inputs to the Refuge. Our theory was that some contaminants might be reduced through the plugging of old open wells, the retirement of certain agricultural land on the Refuge, and identifying off-refuge lands whose change in land use management would benefit the Refuge and targeting them for possible partnerships with the Partners for Fish and Wildlife Program.

Fortunately, the lack of consistent elevated concentrations from the sampling effort negated the need to use the GIS database for the spatial correlation analysis or to determine likely source areas of contaminants. Many of the land use practices we anticipated implementing as a result of the study, were put in practice well before the completion of the study.

Unfortunately, the contractor for the GIS database did not deliver the products on time, which in turn caused a delay in the completion of this study. The products were of poor quality and did not meet expectations. Refuge staff have found limited value in the GIS database created for this study to track information on abandoned wells, land use management, exotic species locations, etc.

SUMMARY

Waterborne concentrations of atrazine, 2,4-D, and alachlor compounds were observed in surface waters entering FHNWR in 1997. In 1999, only one site had a detection of any pesticide compound. Low concentrations of aliphatic hydrocarbons and polycyclic aromatic hydrocarbons were infrequently detected in sediments and benthic invertebrates. Only one organochlorine contaminant (dicamba) was detected and that was found in only one sample.

The study design was not developed to be intensive, and therefore this study does not represent a conclusive evaluation of contaminant sources and loads into FHNWR. However, these data can serve as useful baseline information for possible future investigations.

A major limitation to this study includes the lack of repeat sampling within a time period. Also, we were unable to precisely time sampling with precipitation events. We most likely did not detect the maximum concentrations that occurred during a sampling period. Therefore, our data probably do not represent the full range or duration of pesticide loadings to FHNWR. Any future study that focuses on agricultural chemicals, should consider a daily sampling approach for an extended period. This sampling scheme would provide a better understanding of variability and potentially capture variability associated with rainfall events.

MANAGEMENT ACTIONS

The intermittent flood hydrology of the Neosho River Basin above the John Redmond Reservoir poses serious problems for all management activities on the Refuge. At high pool level, 95 percent of the Refuge may be flooded for extended periods (Research Management Consultants, Inc. 2000). This study has shown that some contaminants are associated with flows into the Refuge and that contaminants accumulate in sediments. Future investigations should take place to determine the extent that mudflats, associated with long term flooding are impacted by contaminants.

The Refuge has approximately 3,917 acres of cropland. Although, limited chemical use is permitted on cropland within the Refuge, it is a concern due to the frequency of flooding and the potential of those chemicals to enter surface water runoff. Several measures have been taken to minimize unintentional impacts. Refuge management initiated the mandatory creation of buffers along streams in agricultural lands on the Refuge beginning in 1996. Most of these are well established at this time. The riparian buffers are 200 feet wide along the Neosho River and 150 feet wide along major drainage ways or tributaries to the river. Some have been allowed to re-establish themselves naturally and others have had some management activities such as tree planting and/or invasive plant control. The buffers serve to control erosion and reduce contaminant loading to the surface waters of the Refuge. The buffers have been phased-in as the agricultural contracts were renewed. In addition to the riparian corridor buffers, management recently implemented native grass borders along crop fields. These will be a 66-foot wide strip of either cool season or warm season native grasses (J. Gamble, pers. comm.). Also, Refuge cropland is usually double cropped, a management approach that combats weed problems and reduces the amount of herbicide applied.

The Refuge has approximately 4,572 acres of wetlands, and when not flooded are filled with waters from the Neosho River and Eagle Creek. It is probable that contaminants are entering the wetlands through the waters used to fill them and therefore the biota. For example, invertebrate populations are important sources of food for most species of fish, wildlife, and waterfowl. Many species require high protein diets for optimal reproduction and the invertebrate component of the diet is often the principal source of protein (Skorupa, *et al.* 1996). Therefore, management should consider monitoring the water for detrimental effects of water based contaminants on the biota of these wetlands. Monitoring should be done on an intense schedule (hourly, daily, weekly) for

some time period using auto-sampling devices. The data gathered would provide more accurate evaluation of agricultural management practices and information useful in modeling the transport and fate of agricultural chemicals on FHNWR.

The Refuge itself is not likely a source of agricultural chemical contamination. However, off-Refuge croplands and streams are the most likely contributors. Minimizing off-Refuge contaminant sources could be addressed through the U.S. Fish and Wildlife Service's Partners for Wildlife Program. Cooperators could be assisted with their efforts to establish vegetative buffers along streams, retire cropland by returning it to wetlands and grasslands, and fencing out riparian areas to keep cattle and their wastes out of streams. These actions would decrease the quantity of agricultural chemicals used on adjacent lands and reduce the amount of contaminant runoff into surface waters entering the Refuge.

Willow tree invasion is a problem in the moist soil wetlands. Mowing, flooding, and periodic mechanical control of vegetation are used to control the growth. The practice of soil scraping or discing may be disturbing lead shot on the Refuge, and potentially mobilize lead to become more bioavailable to ecological receptors, as indicated by the elevated sediment lead concentrations (Table 5). The use of lead shot for waterfowl hunting is now banned and areas of the Refuge are now closed to hunting. Most of the lead discharged into surface waters is rapidly incorporated into suspended and bottom sediments where it remains until disturbed. Willow control methods that do not disturb the sediment/soils of the wetland units and further study should be considered.

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TABLES

Table 1. Compounds and elements analyzed in surface water, sediment and benthic invertebrates, Flint Hills National Wildlife Refuge, Kansas, in 1999.

Organochlorines
2,4-D[1]
2,4-DB[1]
2,4,5-T[1]
alachlor1
alpha BHC[2]
alpha chlordane[2]
azinphos-methyl[1]
beta BHC[2]
chlorpyifos[1]
cis-nonachlor[2]
coumaphos[1]
delta BHC[2]
diazinon[1]
dicamba[1]
dichlorprop[1]
dieldrin[2]
dimethoate[2]
endrin[2]
EPN[1]
ethoprop[1]
famphur[1]
fensulfothion[1]
gamma BHC[2]
gamma chlordane[2]
HCB[2]
heptachlor epoxide[2]
malathion[1]
methyl parathion[1]
mevinphos[1]
mirex[2]
o,p'-DDD[2]
o,p'-DDE[2]
o,p'-DDT[2]
oxychlordane[2]
parathion[1]
p,p'-DDD[2]
p,p'-DDE[2]
p,p'DDT[2]
silvex[1]
total PCBs[2]
toxaphene[2]
trans-nonachlor[2]
trichlorfon[1]

Carbamates[1]
1-naphthol
aldicarb
aldicarb sulfone
aldicarb sulfoxide
baygon
carbaryl
carbofuran
carbofuran 3-OH
methomyl
oxamyl

Trace Elements[3]
aluminum
arsenic
boron
barium
beryllium
cadmium
chromium
copper
iron
mercury
magnesium
manganese
molybdenum
nickel
lead
selenium
strontium
vanadium
zinc

Hydrocarbons
1-methylnaphthalene[4]
1-methylphenanthrene[4]
1,6,7-trimethyl-naphthalene[4]
2-methylnaphthalene[4]
2,6-dimethylnaphthalene[4]
acenaphthalene[4]
ancenaphthene[4]
anthracene[4]
benzo(a)anthracene[4]
benzo(a)pyrene[4]
benzo(b)fluoranthene[4]
benzo(e)pyrene[4]
benzo(g,h,i)perylene[4]
benzo(k)fluoranthene[4]
biphenyl[4]
C1-chrysenes[5]
C1-dibenzothiophenes[5]
C1-floranthenes & pyrenes[5]
C1-fluorenes[5]
C1-naphthalenes[5]
C1-phenanthrenes[5]
C2-chrysenes[5]
C2-dibenzothiophenes[5]
C2-fluorenes[5]
C2-naphthalenes[5]
C2-phenanthrenes[5]
C3-chryzenes[5]
C3-dibenzothiophenes[5]
C3-fluorenes[5]
C3-naphthalenes[5]
C3-phenanthrenes[5]
C4-chrysenes[5]
C4-naphthalenes[5]
C4-phenanthrenes[5]
chrysene[4]
dibenz(a,h)anthacene[5]
dibenzothiophene[4]
fluoranthene[4]
fluorene[4]
indeno(1,2,3-cd)pyrene[4]
n-decane (n-C10)[5]
n-docosane (n-C22)[5]
n-dodecane (n-C12)[5]
n-dotriacontane (n-C32)[5]
n-eicosane (n-C20)[5]
n-heneicosane (n-C21)[5]
n-hentriacontane (n-C31)[5]
n-heptacosane (n-C27)[5]
n-heptadecane (n-C17)[5]
n-hexacosane (n-C26)[5]
n-hexadecane (n-C16)[5]
n-nonacosane (n-C29)[5]
n-nonadecane (n-C19)[5]
n-octacosane (n-C28)[5]
n-octadecane (n-C18)[5]
n-pentacosane (n-C25)[5]
n-pentadecane (n-C15)[5]
n-tetracosane (n-C24)[5]
n-tetradecane (n-C14)[5]
n-tetratriacontane (n-C34)[5]
n-triacontane (n-C30)[5]
n-tricosane (n-C23)[5]
n-tridecane (n-C13)[5]
n-tritriacontane (n-C33)[5]
n-undecane (n-C11)[5]
naphthalene[4]
perylene[4]
phenanthrene[4]
phytane[5]
pristane[5]
pyrene[4]

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1 - water only
2 - water & sediment
3 - water, sediment & benthic invertebrates
4 - benthic invertebrates & sediment
5 - sediment only

Table 2. Atrazine concentrations (in µg/l) in surface water collected from Flint Hills National Wildlife Refuge, Kansas in 1997.

	May	June	August	September
Site 1	0.28	0.79	0.03	0.03
Site 2	1.47	6.53	0.31	0.25
Site 3	0.51	3.71	0.07	NA
Site 4	0.45	9.85	0.55	0.83
Site 5	7.7	10.50*	0.71	0.54
Site 6	18.7*	4.77	0.45	0.1
Site 7	13.09*	8.49	1.2	0.76
Site 8	4.21	6.46	0.6	0.42

NA = Not Analyzed
* = Concentrations were outside the detection range of the test kit and were interpolated by the photometer computer.

Table 3. 2, 4-D compound concentrations (in µg/l) in surface water collected from Flint Hills National Wildlife Refuge, Kansas in 1997.

	May	June	August	September
Site 1	0.21	2.18	0.42	0.4
Site 2	0.13	0.42	0.32	0.35
Site 3	0.22	0.48	0.69	NA
Site 4	0.7	0.74	0.59	0.45
Site 5	0.31	0.35	0.58	0.17
Site 6	2.38	0.46	0.96	0.87
Site 7	0.27	NA	0.57	NA
Site 8	0.17	NA	0.44	NA

NA = Not Analyzed

Table 4. Alachlor compound concentrations (in µg/l) in surface water collected from Flint Hills National Wildlife Refuge, Kansas in 1997.

	May	June	August	September
Site 1	0.14	5.05*	0.07	0.21
Site 2	0.08	3.24	0.41	0.12
Site 3	0.05	0.12	0.01	NA
Site 4	0.15	0.13	0.11	0.05
Site 5	0.23	0.38	0.11	0.12
Site 6	0.6	0.34	0.03	0.05
Site 7	0.33	0.5	0.58	0.23
Site 8	0.2	0.07	0.03	0.03

NA = Not Analyzed
* = Concentrations were outside the detection range of the test kit and were interpolated by the photometer computer.

Table 5. Trace element concentrations (in µg/g dry weight (dw)) in sediment collected on Flint Hills National Wildlife Refuge, Kansas in 1999.

Sample Number	aluminum	arsenic	boron	barium	beryllium	cadmium
FLHSDI01	20854	6.18	<10.0	209	1.95	0.467
FLHSDI02	15184	14.6	<10.0	250	1.86	0.375
FLHSDI04	27145	8.16	10.2	266	2.88	0.427
FLHSDI05	19805	6.06	<10.0	178	1.92	0.307
FLHSDI06	17254	20.1	<10.0	380	2.21	0.351
FLHSDI07	16748	9.12	<10.0	155	1.66	0.222
FLHSDI08	13307	7.63	<10.0	168	1.36	<.200

Sample Number	chromium	copper	iron	mercury	magnesium	manganese
FLHSDI01	22.7	20	21079	ND	4817	399
FLHSDI02	23	15.6	28598	ND	2493	1599
FLHSDI04	26.9	19.3	25486	ND	5267	962
FLHSDI05	19.9	14.7	20082	ND	3485	471
FLHSDI06	20.2	13.3	30645	ND	2435	1829
FLHSDI07	22.8	14	25075	ND	3372	610
FLHSDI08	16.7	13.2	21560	ND	4316	851

Sample Number	molybdenum	nickel	lead	strontium	vanadium	zinc
FLHSDI01	ND	23.4	20.8	78.3	26	74.7
FLHSDI02	ND	26.6	40.4	33.3	44.8	49.3
FLHSDI04	ND	27.4	2408	73	38.2	72.6
FLHSDI05	ND	19.7	17.8	38.7	28.2	56
FLHSDI06	ND	24	62.8	37.5	73.7	44.5
FLHSDI07	ND	23	21	49.4	30.7	56.3
FLHSDI08	ND	18.8	15.4	156	20.9	47.3

ND = Not Detected

Table 6. Trace element concentrations (in µg/g) in benthic invertebrates collected on Flint Hills National Wildlife Refuge, Kansas in 1999.

Sample Number	% Moisture	aluminum		arsenic		boron	
		Dry	Wet	Dry	Wet	Dry	Wet
FLHBII01	86.3	747	102	1.42	0.194	ND	ND
FLHBII02	83.7	709	116	0.992	0.162	ND	ND
FLHBII04	80.2	488	96.4	1.04	0.206	ND	ND
FLHBII05	82.8	439	75.7	0.866	0.149	ND	ND
FLHBII06	81	3419	648	1.29	0.244	2.04	0.387
FLHBII07	80.8	874	168	0.939	0.18	ND	ND
FLHBII08	79.5	1807	371	1.32	0.27	2.01	0.412

Sample Number	barium		beryllium		cadmium		chromium	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
FLHBII01	38.7	5.3	0.1	0.014	0.138	0.019	3.38	0.463
FLHBII02	80.9	13.2	ND	ND	0.209	0.034	2.34	0.382
FLHBII04	44.3	8.75	ND	ND	0.163	0.032	1.66	0.328
FLHBII05	56.4	9.73	0.1	0.017	ND	ND	1.71	0.295
FLHBII06	125	23.6	0.26	0.049	0.159	0.03	6.92	1.31
FLHBII07	66.1	12.7	0.12	0.023	0.185	0.036	2.46	0.473
FLHBII08	47.5	9.74	0.15	0.031	0.109	0.022	3.87	0.794

ND = Not Detected

Table 6. (continued). Trace element concentrations (in µg/g) in benthic invertebrates collected on Flint Hills National Wildlife Refuge, Kansas in 1999.

Sample Number	copper		iron		mercury		magnesium	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
FLHBII01	65.8	9.02	595	81.6	0.368	0.051	1586	217
FLHBII02	80.8	13.2	479	78.2	ND	ND	1637	268
FLHBII04	52.2	10.3	332	65.5	0.277	0.055	1705	337
FLHBII05	62.3	10.7	299	51.5	0.459	0.079	1997	344
FLHBII06	62.1	11.8	1927	365	ND	ND	1771	336
FLHBII07	74	14.2	635	122	0.248	0.048	1786	343
FLHBII08	55.4	11.4	1347	276	0.253	0.052	1729	355

Sample Number	manganese		molybdenum		nickel		lead	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
FLHBII01	153	20.9	ND	ND	1.45	0.199	0.802	0.11
FLHBII02	63.4	10.4	ND	ND	1.63	0.266	0.753	0.123
FLHBII04	72.1	14.2	ND	ND	1.37	0.271	ND	ND
FLHBII05	123	21.2	ND	ND	1	0.172	ND	ND
FLHBII06	314	59.6	ND	ND	2.41	0.457	2.53	0.48
FLHBII07	89	17.1	ND	ND	1.55	0.298	0.753	0.145
FLHBII08	142	29.2	ND	ND	1.41	0.289	1.23	0.253

Table 6. (concluded). Trace element concentrations (in µg/g) in benthic invertebrates collected on Flint Hills National Wildlife Refuge, Kansas in 1999.

Sample Number	selenium		strontium		vanadium		zinc	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
FLHBII01	2.19	0.301	76.3	10.5	1.17	0.16	85.6	11.7
FLHBII02	2.01	0.329	147	24	1.3	0.212	68.3	11.2
FLHBII04	2.71	0.535	94.2	18.6	1.34	0.265	74.2	14.7
FLHBII05	1.45	0.249	73.2	12.6	1.12	0.193	75	12.9
FLHBII06	2.2	0.418	101	19.2	7.4	1.4	71.2	13.5
FLHBII07	1.76	0.337	115	22.1	0.9	0.173	69.3	13.3
FLHBII08	2.03	0.416	77.2	15.8	2.24	0.459	77.7	15.9

Table 7. Trace element concentrations (in mg/l) in surface water samples collected on Flint Hills National Wildlife Refuge, Kansas in 1999.

Sample Number	aluminum	arsenic	boron	barium
FLHWTI01	1.37	0.0077	0.082	0.137
FLHWTI02	0.0847	ND	0.072	0.0734
FLHWTI04	3.44	0.0137	0.064	0.212
FLHWTI05	0.147	ND	0.063	0.0972
FLHWTI06	7.94	ND	0.057	0.514
FLHWTI07	1.11	ND	0.07	0.0937
FLHWTI08	0.768	0.008	0.057	0.0941

Sample Number	beryllium	cadmium	chromium	iron
FLHWTI01	ND	ND	ND	2.21
FLHWTI02	ND	ND	ND	0.059
FLHWTI04	0.0005	ND	ND	4.17
FLHWTI05	ND	ND	ND	0.399
FLHWTI06	0.0016	ND	0.0081	8.69
FLHWTI07	ND	ND	ND	1.22
FLHWTI08	ND	ND	ND	0.924

ND = Not detected

Table 7. (continued). Trace element concentrations (in mg/l) in surface water samples collected on Flint Hills National Wildlife Refuge, Kansas in 1999.

Sample Number	mercury	magnesium	manganese	molybdenum
FLHWTI01	ND	5.78	0.547	0.0045
FLHWTI02	ND	6.66	0.0077	ND
FLHWTI04	ND	11.3	0.617	ND
FLHWTI05	ND	7.86	0.703	ND
FLHWTI06	ND	5.62	0.858	ND
FLHWTI07	ND	8.28	0.146	ND
FLHWTI08	ND	10.5	0.236	ND

Sample Number	nickel	lead	selenium	strontium
FLHWTI01	ND	ND	ND	0.221
FLHWTI02	ND	ND	ND	0.21
FLHWTI04	0.0093	ND	ND	0.434
FLHWTI05	ND	ND	ND	0.204
FLHWTI06	0.017	0.026	ND	0.176
FLHWTI07	ND	ND	ND	0.252
FLHWTI08	ND	ND	ND	0.281

Table 7. (concluded). Trace element concentrations (in mg/l) in surface water samples collected on Flint Hills National Wildlife Refuge, Kansas in 1999.

Sample Number	vanadium	zinc
FLHWTI01	0.0083	ND
FLHWTI02	ND	ND
FLHWTI04	0.0215	0.0183
FLHWTI05	ND	ND
FLHWTI06	0.039	0.0313
FLHWTI07	0.0052	ND
FLHWTI08	ND	ND

Table 8. Soil or sediment element concentrations from the U.S. Except as noted, concentrations are in µg/g dry weight (dw).

	Location				
Element	Conterminous U.S. soils (a,e)	Western U.S. soils (a,e)	Northern Great Plains soils (b,e,)	North-Central U.S. sediments (c,i)	Western U.S. DOI study area sediments (d,g)
aluminum	4.7%	5.8%	5.6%	NA	1.8-9.8%
antimony	0.48	0.47	NA	NA	NA
arsenic	5.2	5.5	7.1	4.4 (h), 2.4 (i)	0.6-120
barium	440	580	1100	NA	67-220
beryllium	0.63	0.68	1.6	NA	ND-3.0
boron	26	23	41	NA	ND-390
cadmium	NA	NA	NA	0.52 (h), 0.26 (i)	NA
chromium	37	41	45	NA	3.0-330
copper	17	21	19	NA	3.0-520
iron	1.8%	2.1%	2.1%	Na	0.4-6.3%
lead	16	17	16	13 (h), 6.6 (i)	ND-500
magnesium	0.44%	0.74%	0.66%	NA	0.04-4.8%
manganese	330	380	460	NA	66-4500
mercury	0.58	0.046	0.023	0.03 (h), 0.03 (i)	ND-18
molybdenum	0.59	0.85	308	NA	ND-73
nickel	13	15	18	NA	ND-170
selenium	0.26	0.23	0.45	0.89(h), 0.52 (i)	ND-85
strontium	120	200	NA	NA	59-1600
tin	0.89	0.9	160	NA	NA
vanadium	58	70	54	NA	5-310
zinc	48	55	63	NA	10-1600

(a) Shacklette and Boerngen 1984
(b) Severson and Tidball 1979
©) Martin and Hartman 1984
(d) Severson *et al.* 1987 and Harms *et al.* 1990
(e) geometric means
(f) unspecified means
(g) only range of values given
(h) mean for pothole wetlands
(i) mean for riverine wetlands

Table 9. Composition of sediment samples collected on Flint Hills National Wildlife Refuge, Kansas in 1999.

Sample Number	% Moisture	% Total Organic Carbon	% Grain Size			Sediment Type
			Sand	Silt	Clay	
FLHSDI01	62.6	<3.14	1.98	30.7	67.3	Clay
FLHSDI02	36.4	<.940	21.9	40.1	38	Clay loam
FLHSDI04	42.3	<1.96	1.46	39.4	59.1	Clay
FLHSDI05	40.8	<1.44	3.12	57.9	38.9	Silty clay loam
FLHSDI06	37.4	<1.09	12	54.4	33.6	Silty loam
FLHSDI07	40.6	<1.37	12.7	51.3	36	Silty loam
FLHSDI08	45.9	<.960	10.6	67.3	22	Silt

Table 10. Aliphatic hydrocarbon concentrations (in µg/g dry weight) in sediment samples collected at Flint Hills National Wildlife Refuge, Kansas in 1999.

Sample Number	n-decane n-C10	n-tetradecane n-C14	n-pentadecane n-C15	n-hexadecane n-C16	n-heptadecane n-C17
FLHSDO01	0.029	0.0826	0.0804	0.114	0.152
FLHSDO02	0.0264	ND	0.0248	ND	0.0388
FLHSDO04	0.0247	ND	0.0212	ND	0.0494
FLHSDO05	0.0223	ND	0.0377	ND	0.12
FLHSDO06	0.0212	ND	ND	ND	0.0407
FLHSDO07	0.0221	ND	0.0408	0.0187	0.0544
FLHSDO08	0.023	ND	0.0518	0.0422	0.094

Sample Number	n-octadecane n-C18	n-nonadecane n-C19	n-eicosane n-C20	n-heneicosane n-C21	n-docosane n-C22
FLHSDO01	0.0246	0.116	0.0357	0.0826	0.0759
FLHSDO02	ND	0.0233	0.0248	0.0792	0.0543
FLHSDO04	ND	ND	0.0247	0.0406	0.06
FLHSDO05	0.0188	0.0582	0.0394	0.0856	0.127
FLHSDO06	ND	ND	0.0179	0.0293	0.0472
FLHSDO07	0.0204	0.0323	0.0306	0.0578	0.0544
FLHSDO08	0.0576	0.0806	0.0729	0.0979	0.0825

ND = Not Detected

Table 10. (concluded). Aliphatic hydrocarbon concentrations (in µg/g dry weight) in sediment samples collected at Flint Hills National Wildlife Refuge, Kansas in 1999.

Sample Number	n-tricosane n-C23	n-tetracosane n-C24	n-pentacosane n-C25	n-hexacosane n-C26	n-heptacosane n-C27
FLHSDO01	0.183	0.0759	0.212	0.0781	0.446
FLHSDO02	0.202	0.073	0.152	0.0652	0.264
FLHSDO04	0.104	0.0617	0.122	0.0582	0.247
FLHSDO05	0.342	0.223	0.788	0.274	0.805
FLHSDO06	0.0765	0.0456	0.0961	0.0407	0.228
FLHSDO07	0.122	0.0595	0.255	0.0629	0.68
FLHSDO08	0.169	0.0768	0.288	0.0921	0.557

Sample Number	n-octacosane n-C28	n-nonacosane n-C29	n-triacontane –C30	– hentriacontane n–C31	n-dotriacontane n–C32
FLHSDO01	0.152	2.25	0.0893	0.58	ND
FLHSDO02	0.0839	0.668	0.045	0.326	0.0171
FLHSDO04	0.109	0.511	0.0758	0.494	0.0388
FLHSDO05	0.24	1.11	0.134	0.805	0.0514
FLHSDO06	0.0814	0.505	0.0391	0.293	0.0179
FLHSDO07	0.117	1.34	0.0561	0.578	ND
FLHSDO08	0.146	1.57	0.0653	0.71	ND

Sample Number	n-tritriacontane –C33	–tetratriacontane –C34	phytane	pristane
FLHSDO01	0.123	ND	0.0424	0.0268
FLHSDO02	0.073	ND	0.0202	0.124
FLHSDO04	0.122	ND	ND	ND
FLHSDO05	0.308	0.0223	0.0308	ND
FLHSDO06	0.0717	ND	ND	ND
FLHSDO07	0.143	ND	0.017	0.0221
FLHSDO08	0.175	0.025	0.0557	0.0461

Table 11. Indices used to determine petrogenic or biogenic origin of aliphatic hydrocarbons in sediment collected on Flint Hills National Wildlife Refuge, Kansas in 1999. Values from Table 9 that are "ND" were calculated as "0" in the formulas.

Sample Number	C17/ Pristane Ratio	C18/ Phytane Ratio	Odd/ Even Ratio	Pri/Phy	C16 Ratio	CPI
FLHSDO01	5.7	0.6	5.6	0.63	43.2	11.5
FLHSDO02	0.31	0.0202	4.8	6.2	0	6.7
FLHSDO04	0.0494	0	5.1	0	0	4.3
FLHSDO05	0.12	0.6	4.1	0	0	4.3
FLHSDO06	0.0407	0	4.3	0	0	0.86
FLHSDO07	2.5	1.2	2.2	1.3	199.3	11.4
FLHSDO08	2	1	2.2	0.83	105.1	9.5

Table 12. Polycyclic aromatic hydrocarbon concentrations (in µg/g dry weight) in sediment collected at Flint Hills National Wildlife Refuge, Kansas in 1999.

Sample Number	benzo (a) anthra-cene	benzo (a) pyrene	benzo (b) fluoran-thene	benzo (e) pyrene	phenanthrene	naphthalene	perylene
FLHSDO01	ND	ND	ND	ND	ND	0.0491	0.0246
FLHSDO02	ND	ND	ND	ND	0.0155	0.0357	ND
FLHSDO04	ND	ND	ND	ND	ND	0.0406	ND
FLHSDO05	ND	ND	ND	ND	ND	0.0428	0.0163
FLHSDO06	0.024	0.02	0.0244	0.02	ND	0.0407	ND
FLHSDO07	ND	ND	ND	ND	ND	0.0374	ND
FLHSDO08	ND	ND	ND	ND	ND	0.0422	ND

ND = Not Detected

Table 13. Polycyclic aromatic hydrocarbon concentrations (in µg/g dry weight) in benthic invertebrates collected at Flint Hills National Wildlife Refuge, in 1999.

Sample Number	% Moisture	naphthalene	perylene
FLHBIO01	84.9	ND	ND
FLHBIO02	80.7	ND	ND
FLHBIO04	78.4	ND	0.088
FLHBIO05	81.3	ND	ND
FLHBIO06	82.7	0.0636	0.0867
FLHBIO07	80.3	0.0558	0.102
FLHBIO08	83.7	ND	ND

ND = Not Detected